



10/526 982
Rec'd PCT/PTO 07 MAR 2005
GB 2003 / 0 0 3 8 8 8



#2

INVESTOR IN PEOPLE

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

REC'D 20 OCT 2003


WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

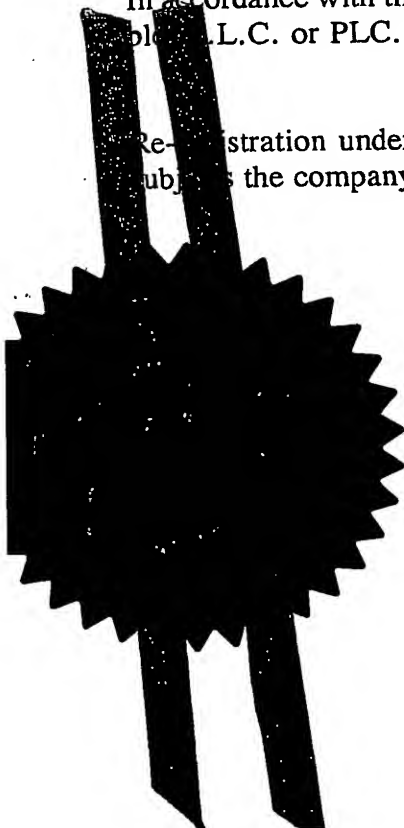
In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

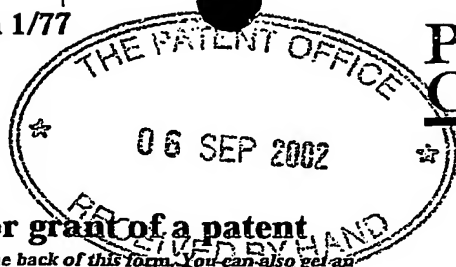
In accordance with the rules, the words "public limited company" may be replaced by p.l.c., pl.c., L.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed 

Dated 2 October 2003





The
Patent
Office

07 SEP 11 E746500-0 D02490
P01/7 00 0.00 0220755.3
1/77

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP9 1RH

1. Your reference

SAH02411GB

2. Patent application number

(The Patent Office will fill in this part)

0220755.3

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Cambridge University Technical
Services Ltd
The Old Schools
Trinity Lane
Cambridge
CB2 1TS

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

Terahertz Spectroscopy

5. Name of your agent (if you have one)

Gill Jennings & Every

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Broadgate House
7 Eldon Street
London
EC2M 7LH

Patents ADP number (if you know it)

745002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77

Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description 7

Claim(s)

Abstract

Drawing(s)

5 + 5 *UK*

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents
(please specify)

NO

11. For the applicant
Gill Jennings & Every

I/We request the grant of a patent on the basis of this application.

Signature

Date

6 September 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

HALEY, Stephen

020 7377 1377

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

TERAHERTZ SPECTROSCOPY

Over the past few years, there has been much interest in developing the technique of difference spectroscopy for the investigation of photo-biological systems. Examples of such systems include bacteriorhodopsin and rhodopsin, as well as the study of photosynthetic reaction centers in bacteria and plants. The principle behind difference spectroscopy consists of recording infrared spectra (of, for example, a protein) in two different states, before and after applying an external perturbation such as light. The difference is then calculated, and only vibrational modes that change in intensity or frequency are identified in the difference spectrum. Signals that do not originate from groups affected by the perturbation are subtracted out. This technique is particularly effective in probing minute structural differences between two states.

Light-induced difference spectroscopy (based on Fourier transform infrared (FTIR) technology) has been developed and applied successfully to investigate the structural changes associated with individual bonds of chromophores and proteins. The detection sensitivity (defined as $\Delta T/T$, where T is the transmission coefficient) achieved in the mid-infrared frequency range is 10^{-5} - 10^{-6} , at fixed delay and frequency, although greater sensitivity is required to apply difference spectroscopy to other important photo-biological systems. In the far-infrared, however, the poor performance of FTIR spectrometers, owing to the lack of suitable sources and detectors, makes it impractical to develop a FTIR difference spectroscopy system.

Recent advances in terahertz (THz) time-domain spectroscopy have, though, stimulated interest in developing light-induced THz difference spectroscopy. Key benefits of such spectroscopy include the acquisition of time-resolved data and coherent detection. These give the amplitude and phase of the THz field, rather than simply the laser intensity. The dynamic range of coherent THz detection has been reported to be 10^5 - 10^6 , corresponding to an intensity range of 10^{10} - 10^{12} . Such a high dynamic range together with the intrinsic advantage of time resolved coherent detection make the THz time-domain system attractive for differential spectroscopy.

There has also been proposed differential THz time-domain spectroscopy for the characterization of thin dielectric films. In this approach, a mechanical shaker is used to exchange rapidly the sample of interest and a reference sample at a frequency of 20 - 100 Hz. The small difference between the THz pulses transmitted through sample and reference was monitored with a lock-in amplifier. Extremely high

sensitivity, of the order $\Delta T/T \approx 10^{-9}$, is apparently possible but the requirement for a mechanical shaker limits the practicality of the device and makes it difficult to control and potentially unreliable.

5 According to the present invention there is provided a terahertz spectroscopy system comprising:

a terahertz source for exciting, in use, a sample with a pulse of radiation in the terahertz frequency range;

10 excitation means for providing excitation energy in the form of an electromagnetic or acoustic wave during illumination of the sample by the terahertz source;

a terahertz sensor for receiving energy from the illuminated sample; and

processing means for receiving signals from the terahertz sensor and processing them to provide an output representative of the terahertz spectrum received by the sensor.

15 The excitation means may be a laser and may be a low power laser. The laser may also provide the terahertz source.

Optical components may be provided in the system in order to focus the terahertz radiation onto the sample and also onto the terahertz sensor.

20 Means may be provided for controlling the direction of the exciting energy to scan it across the surface of the sample in use. Corresponding means may be provided to control the illumination of the terahertz radiation in order to enable scanning of this also across the sample.

25 There may also be provided means for focussing or localising the exciting energy in order to control its spatial resolution and hence control the overall spatial resolution of the system.

An example of the present invention will now be described with reference to the accompanying drawings, in which:

30 Figures 1a and 1b are graphs showing the output from an example system according to the present invention when measuring a semiconductor surface and an output of an example system according to the invention showing peak amplitude versus time delay;

Figure 2 is a graph showing measured terahertz signal transients for the same semiconductor material as employed in figure 1 for both unexcited (open circles) and excited (lines) samples;

Figure 3 is a diagram showing a molecular structure of a copper dye molecule sample employed in a measurement using an example system of the present invention;

5 Figure 4 shows two graphs indicating outputs of an example system according to the present invention when measuring the sample of figure 3;

Figure 5 is a plan view of a sample being illuminated by the system of the present invention;

Figure 6 is a side schematic diagram showing the system of the present invention; and

10 Figure 7 shows a plan view of a semiconductor sample and an output of the system according to the present invention showing clearly the increased resolution of the system as it passes from a first to second material.

Referring now to the figures, an example system according to the present invention will be described, together with two example experiments using that system.

15 Referring to figure 6, a system 1 according to the present invention has a terahertz source 2 which is focussed through optical optics 3 onto a sample 4. The sample 4 is also illuminated by an exciting energy source 5, which in this case a pumped Ti:sapphire laser. Additional optional optics 6 focus terahertz radiation passing through the sample 4 to a terahertz sensor 7 which provides an output to

20 processing means 8. As can be seen from figure 5, the terahertz radiation generated by the terahertz source 2, which may be the laser, can be scanned across the surface of the sample 4 whilst the laser beam 5 is also scanned within the confines of the spot defining the terahertz radiation, such that the whole surface of the sample can be

25 evaluated in a controlled manner

Much of the arrangement of a spectroscopy system according to the invention is similar to that for visible-pump-THz-probe experiments. The laser 6 is provided and produces visible/near-infrared pulses of, in this example, 12 fs duration at a centre wavelength of 790nm. The output is split into three parts: a 250 mW beam is used to

30 excite a sample with a focus diameter of 300µm at a variable time delay with respect to the THz pulse; a 250 mW beam is focused onto the surface of a biased Si-GaAs emitter for THz generation; and the remaining 25mW serves as the probe beam for electro-optic detection using a 1-mm-thick ZnTe crystal.

The laser energy used to excite the samples is only a few nJ, rather than the few μJ used in most pump-probe experiments. This feature has additional benefits in that low energy pulses are less likely to damage the samples under investigation, which is of a particular concern for some biomedical samples.

5 This light-induced THz time-domain difference spectrometer system of the invention can be operated in two ways. The first, and simplest, approach is to use the THz spectrum of the sample in its ground state (without laser excitation) as the reference, and compare this with the spectrum of the sample under laser excitation. The latter can be achieved by electrically chopping the THz beam 2 whilst maintaining
10 constant pump laser excitation. The difference THz spectrum is then calculated, and only vibrational modes that change in intensity or frequency are detected in the difference spectrum. Signals not originating from groups affected by the laser excitation are subtracted out.

In the second approach, if the photogenerated process under investigation is
15 fast and highly reproducible, the difference THz time-domain spectrum is measured directly, with a much higher sensitivity. In this case, the pump beam 5 exciting the sample is chopped by a mechanical chopper whilst the THz beam 2 is kept constant. The idea is to monitor the small THz transmission difference between the two sample states by alternately measuring the THz transmission through the excited and
20 unexcited sample, and monitoring the difference signal with a lock-in amplifier. Owing to the intrinsic advantage of the coherent THz generation and detection, detection levels of the order $\Delta T/T \approx 10^{-8}$ can be demonstrated, which is already 2 – 3 orders of magnitude better than the performance of known FTIR spectroscopy systems.

Two examples of use of the present invention will now be described to aid
25 understanding of its benefits.

Example one, semiconductor sample. In order to evaluate the performance of the light-induced THz time-domain spectrometer of the invention, Si-GaAs and HR-silicon wafers were studied using the second approach discussed above. Fig. 1
30 (a) shows the measured THz signal without the pump laser pulse and the differential THz signal 5 ps after visible laser excitation for Si-GaAs. The amplitude of the differential THz signal is less than 2 % of the original THz signal because only a 2 nJ pulse was used for excitation, corresponding to an energy density of about $3 \mu\text{J}/\text{cm}^2$. The peak amplitude of the differential THz pulse was monitored as a function of time

after the visible laser excitation and is plotted in Fig. 1 (b). A 50 ps lifetime was calculated by fitting the experimental results.

The differential THz signal arrives at the detector about 100 fs later than the original THz signal, as shown in Fig.1 (a). This can be explained as follows. The generated THz pulse is collected and focussed onto the sample surface by two parabolic mirrors. Owing to diffraction during the THz wave propagation, the lower frequency components of the THz pulse will focus to a larger spot size at the sample surface than the higher frequency components. The visible pump laser has a spot diameter of 300 μ m and only this pumped area of the sample will produce the differential THz signal. The spatial confinement of the differential THz pulse in the pump area thus acts as a spectral filter, shifting the frequency distribution of the transmitted THz pulse towards higher frequency. This reshapes the THz waveform and, owing to the normal dispersion, slows the THz pulse down so that it arrives at a later time. The shape and peak position of the differential THz signal can be well simulated by applying a high-pass digital filter to the original THz signal, confirming that the effect of a spectral filter is to cause the later arrival of the differential THz pulse.

In contrast to our observations here, Schall et al. observed the THz pulse to arrive earlier when transmitted through an optically excited Si-GaAs wafer. This is a result of the different experimental arrangement used. It has been known to measure the THz pulses transmitted through an unexcited and a continuously excited GaAs wafer. In this case, the frequency-dependent transmission and phase shift at the air-GaAs (excited) interface has a substantial contribution to the observed earlier arrival of the THz pulse. Indeed the earlier arrival of the THz pulse for excited HR-silicon wafers is shown in Fig. 2. For a silicon wafer the lifetime of the photo-generated carriers is much longer than the time interval between two successive optical pulses (12 ns). A much larger differential THz signal is observed owing to the accumulation of photo-generated carriers in the silicon. Considering that HR-silicon is widely used in THz time-domain spectroscopy experiments, care must be taken to avoid the frequency-dependence of the transmission and phase shift caused by long-lived photo-generated carriers. Note that the effective spot size of the pump beam on the sample surface in this case is much larger owing to the diffusion of the photo-generated electrons.

In summary, for GaAs wafers, we directly measured the differential THz signal resulting from optical excitation. The differential signal is only a small fraction (1 – 2 %) of the original THz signal, therefore, the contribution from the frequency-dependent transmission and phase shift at the interface is much smaller for GaAs than HR-silicon. The main contribution to the differential THz signal is thus from the spectral filter owing to the spatial confinement of the THz pulse in the pump area.

Example two, copper pathancyonine pellet. Pathancyonines are important dye molecules with excellent light harvesting capabilities, and their biomedical applications have been extensively investigated. The molecular structure of copper pathancyonine (CuPc) is shown in Fig. 3. The optical absorption of CuPc peaks at 678 nm and overlaps with the spectrum of the pump laser pulse (centre wavelength 790 nm, bandwidth 100nm). Fig. 4 shows the THz transient transmitted through a CuPc pellet measured in the presence and absence of visible laser excitation. The main THz pulses measured with and without laser excitation are almost identical, suggesting that most frequency components in the absorption spectrum do not change under laser excitation. However, the smaller amplitude ripples after the main pulse in the time domain are different, indicating that some absorption features are changed by the laser excitation. The Fourier transforms of the measured THz transients are calculated and the ratio of their amplitudes is plotted in Fig. 4, together with the relative phase difference. We observe features at 1.08 THz and 1.26 THz. This result represents evidence of a light-induced vibrational mode change in the THz frequency range.

We do not believe that the observed change is results from the mobile electrons, which is the main cause for the differential THz signal in semiconductors. Instead, the observed peak is due to the change in the environment surrounding the vibrational modes. The energy associated with vibration modes in the THz frequency range is about 4 meV, corresponding to a temperature difference (kT) of 47 °C. Therefore a few degrees change in temperature is sufficient to cause substantial change in either the intensity or the frequency of the THz vibrational modes.

The present invention has significant implications for THz medical imaging. The resolution of a THz imaging system is ultimately limited by the wavelength of the THz wave and although near field optics can be used to obtain higher resolution images, this can not be applied to in vivo THz imaging beneath, for example, the surface of skin. As is provided by the present invention, the effective spot size of a THz pulse can be spatially confined to the pump area of a sample, which is determined by the

focussed size of the visible pump laser beam. Therefore the resolution of a differential THz imaging system is ultimately limited by the spot size of the visible pump beam rather than the THz wavelength.

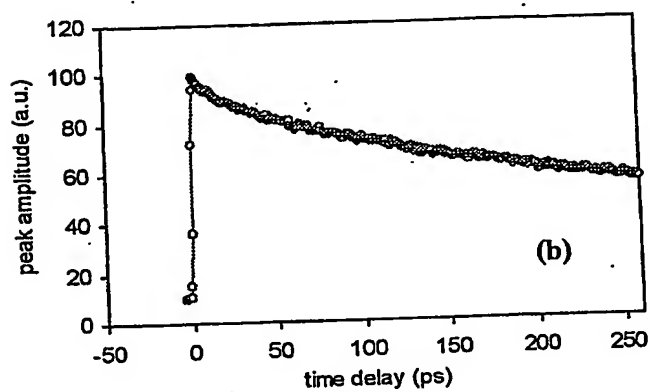
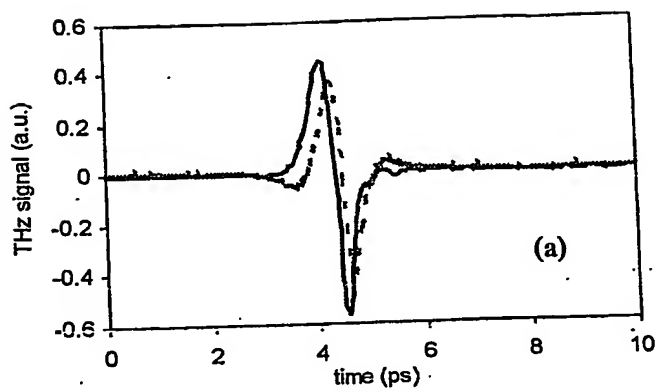


Fig 1.

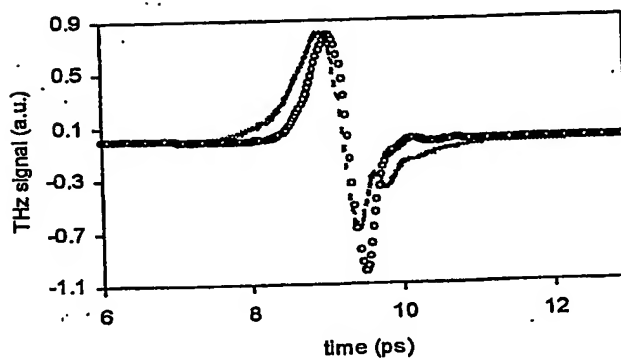


Fig 2.

2/5

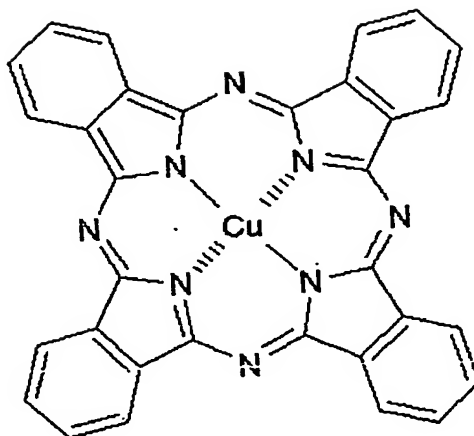


Fig. 3

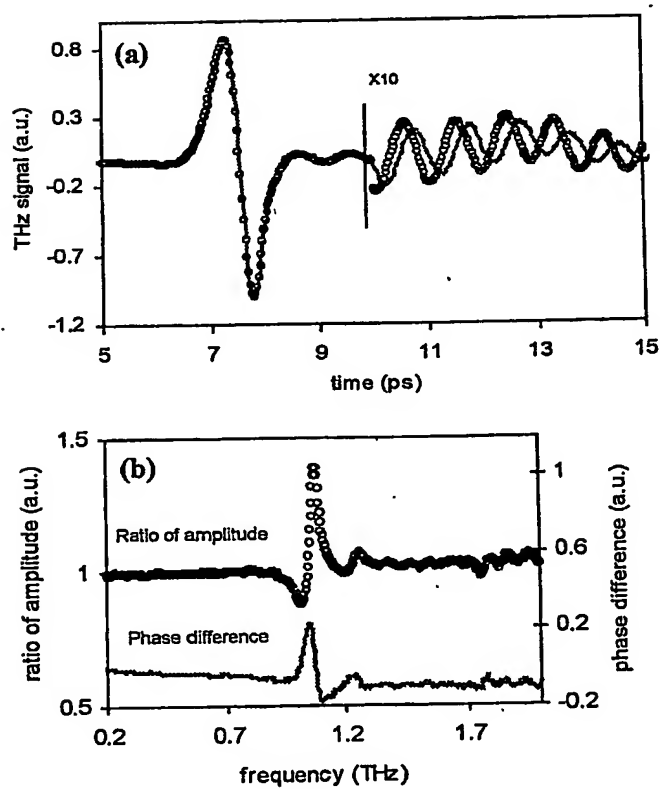
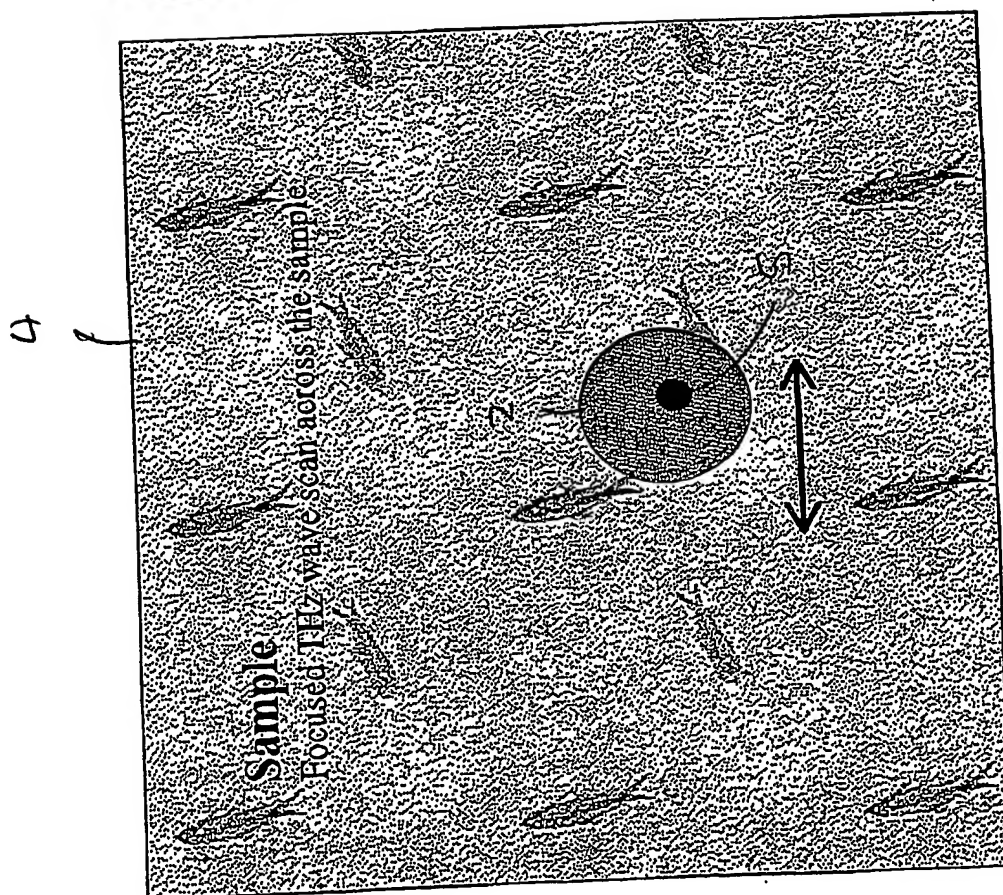
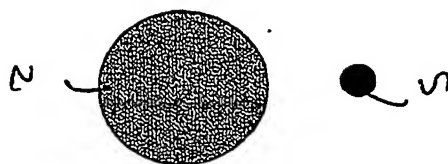


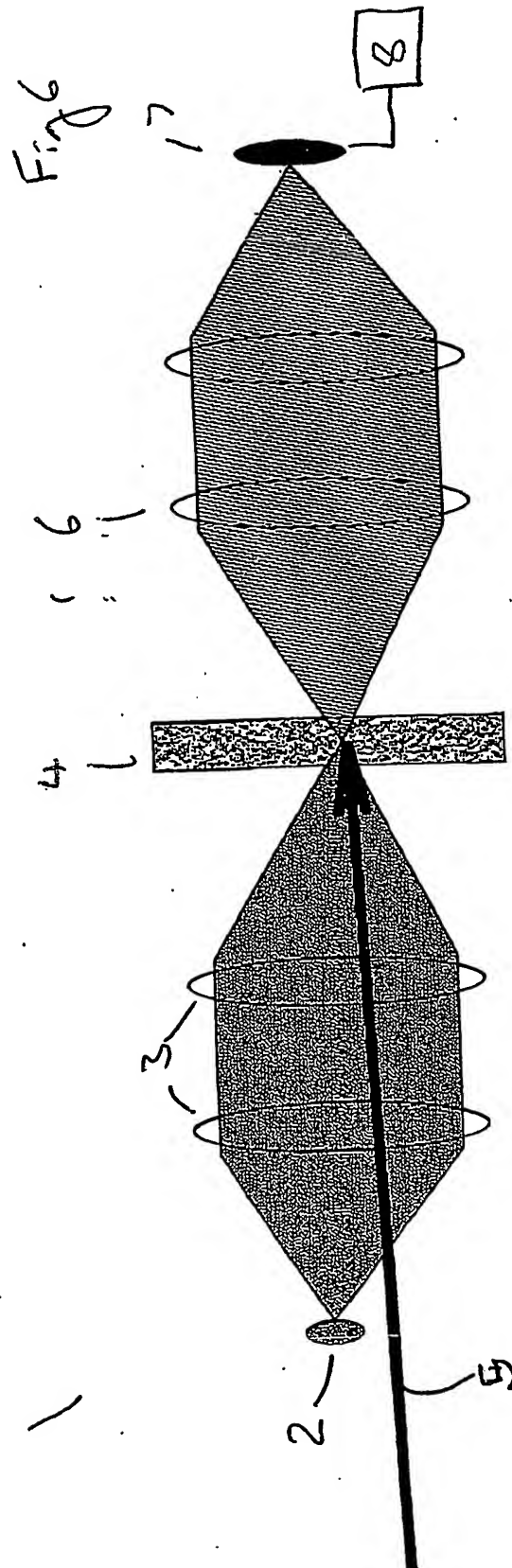
Fig. 4

THz spot size
1THz $\geq 150\mu\text{m}$

laser spot size
Green $< 1.0\mu\text{m}$

Fig 5





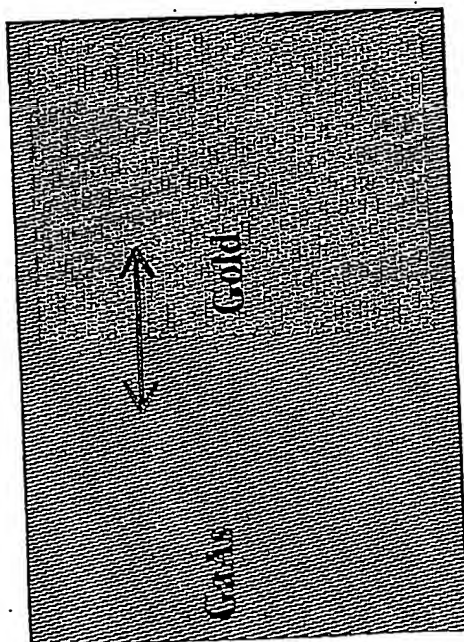
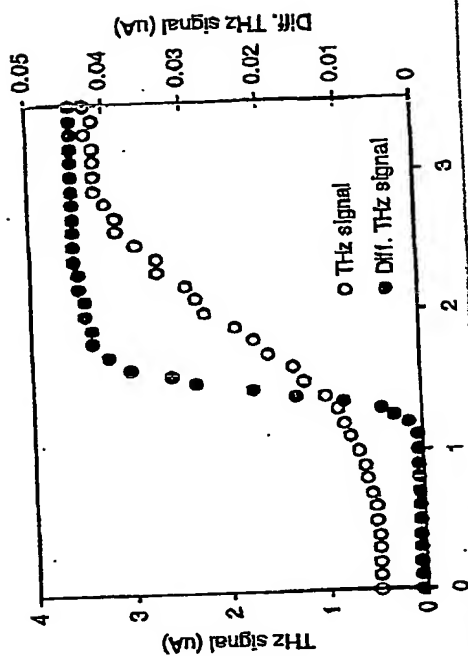


Fig 7